

A fourfold coordinated point defect in silicon

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Due to their technological importance, point defects in silicon are among the best studied physical systems. The experimental examination of point defects buried in bulk is difficult and evidence for the various defects usually indirect. Simulations of defects in silicon have been performed at various levels of sophistication ranging from fast force fields to accurate density functional calculations. The generally accepted viewpoint from all these studies is that vacancies and self interstitials are the basic point defects in silicon. We challenge this point of view by presenting density functional calculations that show that there is a new fourfold coordinated point defect in silicon that is lower in energy.

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The stability of crystalline silicon comes from the fact that each silicon atom can accommodate its four valence electrons in four covalent bonds with its four neighbors. The traditional point defects in silicon, the vacancy and the various interstitials, are obtained by taking out or adding atoms to the crystal and thus all destroy fourfold coordination. A relatively high defect formation energy for these defects is the consequence. In addition there is a point defect, that conserves the number of particles, the Frenkel pair, consisting of a vacancy and an interstitial. If the vacancy and the interstitial are close, the formation energy of a Frenkel pair is less than the sum of an isolated vacancy and interstitial (Table I). Nevertheless the formation energy is still considerable since again bonds are broken. Figure 1 shows a novel defect configuration that has, in contrast to all other point defects, perfect fourfold coordination and will therefore be called Four Fold Coordinated Defect (FFCD).

Using state of the art plane wave density functional theory (DFT) calculations we will now present evidence that the formation energy of the FFCD of 2.4 eV is lower than the formation energy of all other known point defects both in intrinsic and doped silicon. Even though several calculations of this type were published for the traditional defects, we have decided to repeat them for several reasons. a) All these calculations take advantage of error cancellations to obtain energy differences that are more precise than the total energies themselves. This cancellation is obviously best if all the total energies that are compared are calculated with exactly the same method. b) Most DFT calculations used the basic Local Density Approximation (LDA) whereas we used a more precise General Gradient Approximations [1]. c) As was recently shown [2] cells of at least 216 atoms are required for a reasonable convergence. Most published calculations were done with smaller cells. d) We constructed very accurate pseudopotentials [3] based on atomic calculations with the same density functional as

used in our target calculation and we afforded a very large plane wave basis set (25 Ry for the LDA and 35 Ry for the GGA calculations). e) The point defect formation energies in doped silicon were up to now obtained in an approximate way by combining density functional total energy results with the concept of a chemical potential that varies as a function of doping across the experimental band gap of 1.12 eV of silicon [5,4]. We have modeled the effect of doping in a coherent way for both n and p type doped silicon by including explicitly two doping atoms (aluminum and phosphor) in our 216 atom supercell. This procedure leads of course to high doping concentrations for any reasonable size of our computational cell, but by treating coherently and accurately the extreme cases of high and zero doping we can expect the numbers for more moderate doping concentrations to lie in between these results.

Table I shows all the total energy results. We have included in our compilation all defects that have been classified as being low in energy in previous calculations [4–7], i.e. the split (110) X interstitial, the hexagonal H interstitial and the vacancy. In addition we have included a low energy Frenkel pair. In agreement with recent calculation by Needs [8,9], we found that both the tetrahedral interstitial and the caged interstitial [10] are higher in energy and meta-stable. They are therefore not included in the compilation. The energies in Table I do not contain an additional lowering of the energy that is obtained in an infinite crystal by a long range elastic field, which is suppressed in our finite cell. We have calculated this extra elastic energy for a few configurations and found it to be negligible, namely less than .05 eV. Because of the negative U character of the traditional vacancies and interstitials that was postulated with the help of DFT calculations [11,12] and confirmed experimentally [13], the lowest energies are obtained by closed shell configurations. Consequently all calculations were performed without spin polarization.

For the FFCD the bond length and angle do not significantly deviate from their bulk values. Whereas the bond length and angle in the bulk are 2.35 Å and 109 degrees, they respectively vary from 2.25 to 2.47 Å and from 97 to 116 degrees for the bonds formed by the two (red) defect atoms. The fourfold coordination is also visible from the fact that the centers of the maximally localized Wannier functions [14], that give the best possible spatial location of an electron, are located practically exactly in the middle of the bonds established by the geometric distance criteria. The spread of all the Wannier functions is very close to the bulk value of 2.7 a.u. The fact that the LDA and GGA values are very close is not surprising. The simple covalent bonds are very well described by any reasonable density functional and we expect an error of less than a tenth of an eV for this configuration.

Correlation effects are more important for the broken bonds of the other point defects. Hence the DFT values are less reliable than in the case of the FFCD. Recent Quantum Monte Carlo (QMC) calculations [9] for interstitials are in much better agreement with GGA values than with LDA values. We therefore believe that it is unlikely that the energetical ordering predicted by our GGA calculations does not correspond to reality.

The broken bonds of the other point defects are again best visualized by looking at the centers of the maximally localized Wannier functions in the neighborhood of defects. They are located in empty space regions rather than at positions where geometric criteria would predict bonds. Their spread is also significantly larger than the bulk value. In the case of the vacancy the two non-bonding Wannier functions have a spread of 3.6. a.u., for the X interstitial 4.1 a.u. and for the H interstitial 4.7 a.u.. For the Frenkel pair there are two non-symmetric Wannier functions with spreads of 3.5 and 4.4 a.u..

Whereas the classical point defects were all postulated based on simple symmetry considerations, the discovery of this new point defect was made possible by new algorithmic developments. The configurational space was systematically explored by using a modified basin hopping method [16] and an inter-atomic silicon potential [17]. The most promising configurations were then refined with a plane wave electronic structure code [18] developed by J. Hutter et al.. The preconditioned conjugate gradient method [19] was used for the electronic optimization and the DIIS method [20] without any symmetry constraints for the ionic relaxation.

The remarkable fact that the FFCD has not yet been detected experimentally, in spite of its equilibrium concentration which should be many orders of magnitude larger than that of the other defects, is probably due to two factors. First, the experimental search for defects was always guided by theoretical predictions. Second, it is invisible with standard experimental techniques. Because of the perfect fourfold coordination no unpaired electrons exist, a necessary condition for Elec-

tronic Paramagnetic Resonance (EPR) and Electron Nuclear Double Resonance (ENDOR) experiments. Deep Level Transient Spectroscopy (DLTS) requires electronic levels within the gap. Given the perfect coordination this seems unlikely. To examine this point further we have calculated the LDA Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO) splitting. Even though it is known that the gap is not well reproduced by DFT, these levels allow for a qualitative interpretation. The results (Figure 3) show that the FFCD disturbs the band structure indeed much less than the other defects. The FFCD spectrum is also insensitive to the doping level whereas the other spectra are strongly influenced via various Jahn Teller distortions [15] because of their orbital degeneracy.

The basic FFCD can serve as a building block for more extended defects. Two simple defects obtained by combining just two FFCD's in two different ways are shown at the bottom of Figure 1. Their energies of 3.98 eV for the tilted configuration and of 4.17 eV for the parallel configuration are significantly lower than the sum of the energies of two isolated FFCD's.

The consequences of our results are wide ranging. A reexamination of numerous experimental results will be necessary. In particular the tacit assumption that the same kind of defects are responsible both for the electrical and diffusion properties of silicon has been refuted by our calculations. Even though the FFCD does presumably not strongly influence transport properties, it is expected to play an important role in the diffusion properties of silicon.

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- [1] Perdew, J., Burke, K. & Ernzerhof, M., Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett.* **77** 3865 (1996).
 - [2] Puska, M., Pöykkö, S., Pesola, M. & Nieminen, R., Convergence of supercell calculations for point defects in semiconductors: Vacancy in silicon, *Phys. Rev. B* **58** 1318 (1998)
 - [3] Goedecker, S., Teter, M. & Hutter, J., Separable dual space Gaussian Pseudopotentials, *Phys. Rev. B* **54**, 1703 (1996)
 - [4] Lee, W., Lee, S. & Chang, K., First-principles study of the self-interstitial diffusion mechanisms in silicon, *J. Phys.: Condens. Matter* **10** 995 (1998)
 - [5] Car, R., Kelley, P., Oshiyama, A., & Pantelides, S., Microscopic theory of Impurity-defect reactions and impurity diffusion in silicon, *Phys. Rev. Lett.* **52** 1814 (1984)
 - [6] P. Blöchl, E. Smaggiassi, R. Car, D. Laks, W. An-

- dreoni & S. Pantelides, First-principles calculations of self-diffusion constants in silicon, *Phys. Rev. Lett.* **70** 2435 (1993)
- [7] Antonelli, A., Kaxiras, E. & Chadi, D., Vacancy in silicon revisited: Structure and Pressure effects, *Phys. Rev. Lett.* **81** 2088 (1998)
- [8] Needs, R., First-principles calculations of self-interstitial defect structures and diffusion paths in silicon, *J. Phys.: Condens. Matter* **11** 10437 (1999)
- [9] Leung, W., Needs, R., Rajagopal, G., Itoh, S. & Ihara, S., Calculations of silicon self-interstitial defects, *Phys. Rev. Lett.* **83** 2351 (1999)
- [10] S. Clark & G. Ackland, Ab initio calculations of the self-interstitial in silicon, *Phys. Rev. B* **56** 47 (1997)
- [11] Baraff, G., Kane, E., & Schlüter, M., Silicon vacancy: A possible Anderson negative U system, *Phys. Rev. Lett.* **43** 956 (1979)
- [12] Bar-Yam, Y. & Joannopoulos, J., Silicon self-interstitial migration: Multiple paths and charge states, *Phys. Rev. B* **30** 2216 (1984)
- [13] Watkins, G., Troxell, J., Negative-U properties for point defects in silicon *Phys. Rev. Lett.* **4** 593 (1980)
- [14] Marzari, N. & Vanderbilt, D., Maximally localized generalized Wannier functions for composite energy bands, *Phys. Rev. B* **56**, 12847 (1997)
- [15] Bachelet, G., in "*Crystalline Semiconductor Materials and Devices*", edited by P. Butcher and N. March, Plenum Publishing, New York, 1986
- [16] Doye, J., & Wales, D., Thermodynamics of global optimization, *Phys. Rev. Lett.* **80** 1357 (1998)
- [17] Lenosky, T. et al., Highly optimized empirical model of silicon, *Modelling Simul. Mater. Sci. Eng.* **8**, 825, (2000)
- [18] CPMD Version 3.3: developed by J. Hutter, A. Alavi, T. Deutsch, M. Bernasconi, S. Goedecker, D. Marx, M. Tuckerman and M. Parrinello, Max-Planck-Institut für Festkörperforschung and IBM Zürich Research Laboratory (1995-1999)
- [19] M. Payne, M. Teter, D. Allan, T. Arias & J. Joannopoulos, Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients, *Rev. of Mod. Phys.* **64**, 1045, (1992)
- [20] Pulay, P., Convergence acceleration of iterative sequences, *Chem. Phys. Lett.*, **73**, 393, (1980)

TABLE I. The GGA formation energy in eV of the point defects described in the text and depicted in Figures 1 and 2. For comparison the LDA values are given in parentheses for intrinsic silicon.

	p-type	intrinsic	n-type
FFCD	2.45	2.42 (2.34)	2.39
Frenkel	5.65	4.32 (4.26)	5.77
X interstitial	3.33	3.31 (2.88)	2.98
H interstitial	2.80	3.31 (2.87)	3.12
Vacancy	3.01	3.17 (3.56)	3.14

FFCD defect

FFCD defect

Two non-parallel FFCD's

Two parallel FFCD's

FIG. 1. Two views of the FFCD defect (upper part) and two FFCD pairs (lower part). The defects are obtained by moving atoms from the initial positions denoted by black spheres into the final red positions. The centers of the Wannier functions are indicated by the small blue spheres for the single FFCD but omitted for the two pairs. The formation of the FFCD is easily understandable from the upper left panel. There, the upper red atom originates from the upper black position to the left. The swinging movement needed for this displacement does not break the bonds with the upper neighbors, but with the lower ones. A corresponding swing is needed for the lower defect atom. In the final position two new bonds can be formed so that in the end all atoms are again fourfold coordinated.

X interstitial

H interstitial

Vacancy

Frenkel pair

FIG. 2. Classical point defects in silicon: Red atoms indicate atoms in new positions. For the vacancy and the Frenkel pair the empty lattice site is shown by a black sphere. The centers of extended Wannier functions are visualized by increasingly bigger blue spheres, Wannier functions with the typical bulk extension by small blue spheres.

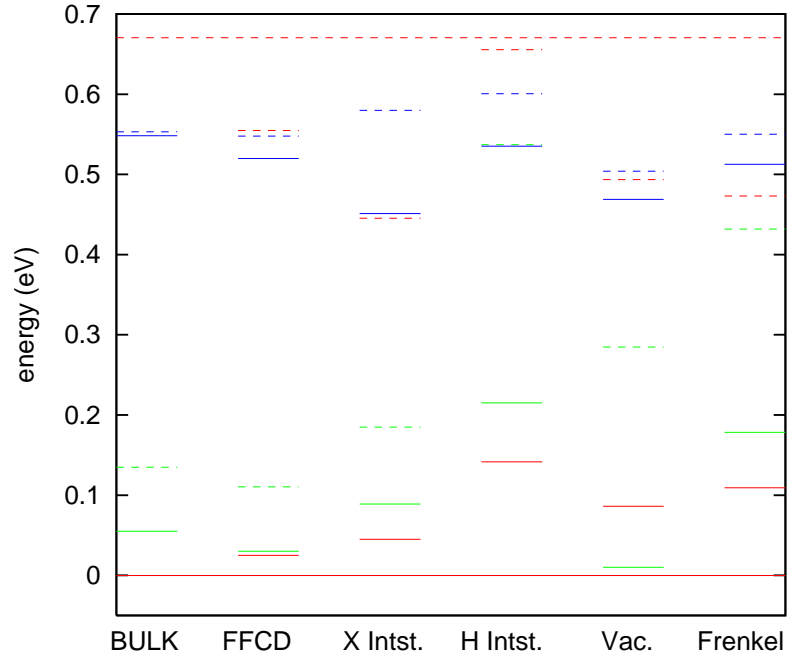


FIG. 3. The HOMO LUMO splitting for the configurations of Table I. The HOMO is denoted by a solid line, the LUMO by a dashed line. Red corresponds to intrinsic silicon, green to p-doped and blue to n-doped silicon. The two levels of intrinsic silicon without defects are drawn over the whole interval.

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